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(54) **METHOD OF MANUFACTURING PRINTED WIRING BOARD**

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method of manufacturing a two-layer metallized polyimide substrate having sufficient insulation reliability even when fine wiring is formed on the substrate.
SOLUTION: In a printed wiring board, a pattern is formed by etching a metal-coated polyimide film formed on one or both surfaces of a polyimide resin film by a dry film forming method and having a first metallic layer composed of Ni, Cu, Mo, Ta, Ti, V, Cr, Fe, Co, and their alloys and a second metallic layer formed on the first metallic layer by electroplating or electroless plating and having conductivity. After etching, the etched surface is oxidized with at least one kind of oxidizing agent selected from among potassium permanganate, potassium dichromate, and hydrogen peroxide.

[Claim(s)]
[Claim 1]The 1st metal layer formed in one side or both sides of a polyimide resin film by the dry type forming-membranes method. The 2nd metal layer that has the conductivity formed with electroplating or nonelectrolytic plating on the 1st metal layer. It is a manufacturing method of a printed-circuit board provided with

the above, and washing processing according the etching surface to an oxidizer is performed after said etching.
[Claim 2]the 1st metal layer -- nickel, Cu, Mo, Ta, Ti, V, Cr, Fe, Co, and ********** -- a manufacturing method of the printed-circuit board according to claim 1 being an alloy which consists of one sort or said metal even if small.
[Claim 3]A manufacturing method of the printed-circuit board according to claim 1 or 2, wherein said oxidizer is an oxidizer containing at least one sort chosen from potassium permanganate, potassium dichromate, and hydrogen peroxide.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the printed-circuit board used as the raw material of electronic parts, such as a printed wired board, a flexible printed circuit board, a TAB tape, and a COF tape.
[0002]
[Description of the Prior Art]Polyimide resin has the outstanding heat resistance, and from it being mechanical, electric, and equal compared with other plastic material also in chemical property. For example, it is used abundantly as an insulating-substrate material for electronic parts, such as a printed wired board (PWB), a flexible printed circuit board (FPC), a tape for tape automated bonding (TAB tape), and COF (Chip on Film).
[0003]Such PWB, FPC, TAB, or a COF tape is obtained by processing at least into one side of a polyimide film the metallic coating polyimide substrate which mainly covered copper as a metallic conductor layer.
[0004]Three layer boards which joined the polyimide film and the metallic foil to this metallic coating polyimide substrate with adhesives, A polyimide film has a two-layer board which formed the metal layer directly, the adhesion of a joining interface is high now, and the two-layer board with which thickness of a polyimide film and a metal layer can be freed attracts attention. Since it is very smooth in a metal-polyimide interface, it is supposed that it is suitable for especially the fine wiring pitch of the two-layer board by the metallizing method.
[0005]However, by the minuteness making of the wiring accompanying the latest high density assembly, the insulation reliability of a printed-circuit board is an important control item, and the

homoiothermal constant humidity bias examination (HHBT examination) is carried out.

[0006]Under such a situation, a metallizing two-layer board, Since the polyimide resin surface is reformed and adhesion power with the 1st metal layer is heightened, even after the associative strength of polyimide and the 1st metal layer performs an etching process strongly, very slightly, a metallic component remains on the polyimide surface and is supposed that it is easy to cause ion migration.

[0007]For example, when a HHBT examination on the voltage 60V is done within the homoiothermal constant humidity chamber of 85 **-85%R.H., Usually, when a wiring pitch was 30 micrometers to the insulation reliability of 1000 hours or more being securable to a predetermined insulation resistance value in the wiring pitch of 40 micrometers, the actual condition was being able to hold insulation reliability only for 1000 or less hours.

[0008]

[Problem(s) to be Solved by the Invention]In order to solve an aforementioned problem, the purpose of this invention is to provide the manufacturing method of the two-layer copper polyimide metallizing board which has insulation reliability sufficient also with fine wiring processed goods.

[0009]

[Means for Solving the Problem]The 1st metal layer by which a method of this invention was formed in one side or both sides of a polyimide resin film by the dry type forming-membranes method in order to solve an aforementioned problem, In a manufacturing method of a printed-circuit board which forms a pattern in a metallic coating polyimide film which has the 2nd metal layer that has the conductivity formed with electroplating or nonelectrolytic plating on it with an etching method, After etching of a wiring board, an oxidizer washes and the etching surface is oxidized.

[0010]the 1st metal layer formed by said dry type forming-membranes method -- nickel, Cu, Mo, Ta, Ti, V, Cr, Fe, Co, and ********** -- even if small, it is preferred that it is one sort or those alloys.

[0011]It is a manufacturing method of a printed-circuit board using an oxidizer containing at least one sort chosen from potassium permanganate, potassium dichromate, and hydrogen peroxide as said oxidizer.

[0012]

[Embodiment of the Invention]As mentioned above, by hydrazine

processing or plasma treatment, a metallizing two-layer board reforms the polyimide surface, and activates a polyimide substrate, and securing combination with the first metal layer is performed. Since this associative strength is strong, in a metallizing two-layer board, the peel strength which can be equal to practical use is revealed.

[0013]However, after forming a pattern by etching, even if it lets the washing process of etching or after that pass, it is considered by the space portion between a lead and leads for the metallic component of the first metal layer of the ultralow volume coupled directly with polyimide to remain to the layer part of polyimide. This invention persons presumed that the metallic component which remains on this surface was one of the causes which causes migration when a HHBT examination is done.

[0014]Then, as a result of examining various surface treatment methods, this invention persons found out that it was more effective to oxidize a residual-metals ion component selectively with an oxidizer rather than having adopted the method of removing thoroughly the metallic component which remains on a surface by etching.

[0015]That is, in order to solve said technical problem, in the printed-circuit board in which the pattern is formed in the metallizing two-layer board by the etching method, the method of carrying out washing processing of the etching surface is provided with an oxidizer after etching. The polyimide film used as an insulating-substrate material in this invention is a hardening film of marketing, such as Du Pont-Toray Kapton V, VN, and E, EN, Ube Industries Upilex-S, and APIKARU by Kaneka Industries, for example.

[0016]Dry type plating can be performed using techniques, such as resistance heating vacuum evaporation, ion plating vacuum evaporation, and cathode sputtering.

[0017]Although physical processing of the chemical treatment by medicine or plasma treatment is employable as a formation method of a polyimide reforming layer, it does not limit to the either.

[0018]As construction material of the 1st metal layer furthermore formed on a polyimide film, metal, such as nickel, Cu, Mo, Ta, Ti, V, Cr, Fe, and Co, or those alloys, those oxides, etc. may be laminated.

[0019]As a detergent which performs ********** of the surface after etching, potassium permanganate, potassium dichromate, hydrogen peroxide, etc. are mentioned, and the oxidizer containing these can be used.

[0020]Below, an example explains the concrete method.

[0021]
[Example](Example 1) One side of the 25-micrometer-thick polyimide film (Du Pont-Toray product name "Kapton 100EN") was processed for 60 seconds in 30% hydrazine- KOH solution. Then, it washed for 10 minutes in pure water, and was made to dry at a room temperature. It laid after desiccation and in the vacuum evaporator, and 10 nm of nickel was vapor-deposited after evacuation to $1x10^{-6}$Torr, further, 8 micrometers of copper was formed by the plating method, and the metallic coating polyimide substrate was obtained.
[0022]40 degrees of ferric chloride solutions use Be (Baume) for the obtained substrate, and it is a 40-micrometer pitch (the linewidth of 20 micrometers). Process it into a comb type pattern (drawing 1) with a space width of 20 micrometers, and 35 **, After potassium hydrate 0.5wt% solution washed potassium permanganate 0.5wt%, within the homoiothermal constant humidity chamber of the atmosphere of 85 **-85%R.H. which rinsed and dried and was installed in the clean room, the bias of 60V was applied to the sample and the insulation reliability examination was done. A result is shown in Table 1.
[0023](Example 2) The insulation reliability examination was done within the homoiothermal constant humidity chamber like Example 1 except having used the comb type pattern as the comb type pattern of a 25-micrometer pitch (the linewidth of 20 micrometers, the space width of 20 micrometers). A result is shown in Table 1.
[0024](Example 3) One side of said polyimide film was installed in the vacuum evaporator, after plasma treatment, in sputtering, 10 nm of nickel was vapor-deposited, further, 8 micrometers of copper was formed by the plating method, and the metallic coating polyimide substrate was obtained. The obtained substrate was processed into the comb type pattern of a 25-micrometer pitch (the linewidth of 20 micrometers, the space width of 20 micrometers), and the insulation reliability examination was done within the homoiothermal constant humidity chamber like Example 1 after that. A result is shown in Table 1.
[0025](Example 4) One side of said polyimide film was installed in the vacuum evaporator, after plasma treatment, in sputtering, 10 nm of Cr(s) were vapor-deposited, further, 8 micrometers of copper was formed by the plating method, and the metallic coating polyimide substrate was obtained. The obtained substrate was processed into the comb type pattern of a 25-micrometer pitch (the linewidth of 20 micrometers, the space width of 20 micrometers), and the insulation reliability examination was done within the homoiothermal constant humidity

chamber like Example 1 after that. A result is shown in Table 1.

[0026](Example 5) One side of said polyimide film was installed in the vacuum evaporator, after plasma treatment, in sputtering, 10 nm of NiCr alloys were vapor-deposited, further, 8 micrometers of copper was formed by the plating method, and the metallic coating polyimide substrate was obtained. The obtained substrate was processed into the comb type pattern of a 25-micrometer pitch (the linewidth of 20 micrometers, the space width of 20 micrometers), and the insulation reliability examination was done within the homoiothermal constant humidity chamber like Example 1 after that. A result is shown in Table 1.

[0027](Example 6) The substrate obtained by obtaining a metallic coating polyimide substrate like Example 5, It is processed into the comb type pattern (drawing 1) of a 25-micrometer pitch (the linewidth of 20 micrometers, the space width of 20 micrometers), After sulfuric acid 2.0wt% solution washed hydrogen peroxide 10.0wt%, within the homoiothermal constant humidity chamber of the atmosphere of 85 **-85%R.H. which rinsed and dried and was installed in the clean room, the bias of 60V was applied to the sample and the insulation reliability examination was done.

[0028]A result is shown in Table 1.

[0029](Example 7) Except having used the 25-micrometer-thick polyimide film (product name by Ube Industries, Ltd. "YUPI REXX S"), the metallic coating polyimide substrate was obtained like Example 5, it was processed into the comb type pattern, and the insulation reliability examination was done within the homoiothermal constant humidity chamber. A result is shown in Table 1.

[0030](Example 8) Except having used the 25-micrometer-thick polyimide film (product name by Kaneka CORP. "APIKARU HP"), the metallic coating polyimide substrate was obtained like Example 5, it was processed into the comb type pattern, and the insulation reliability examination was done within the homoiothermal constant humidity chamber. A result is shown in Table 1.

[0031](Comparative example 1) After processing it into a comb type pattern, except not having washed in potassium hydrate 0.5wt% solution potassium permanganate 0.5wt%, the metallic coating polyimide substrate was obtained like Example 1, it was processed into the comb type pattern, and the insulation reliability examination was done within the homoiothermal constant humidity chamber of atmosphere. A result is shown in Table 1.

[0032](Comparative example 2) The insulation reliability examination was done within the homoiothermal constant humidity chamber like the comparative example 1 except having processed the comb type pattern into a 30-micrometer pitch (the linewidth of 15 micrometers, the space width of 15 micrometers). A result is shown in Table 1.

[0033](Comparative example 3) One side of a 25-micrometer-thick polyimide film (Du Pont-Toray product name "Kapton 100EN"), It installed in the vacuum evaporator, and after plasma treatment, in sputtering, 10 nm of nickel was vapor-deposited, further, 8 micrometers of copper was formed by the plating method, and the metallic coating polyimide substrate was obtained. After processing the obtained substrate into the comb type pattern of a 40-micrometer pitch (the linewidth of 15 micrometers, the space width of 15 micrometers), the insulation reliability examination was done within the homoiothermal constant humidity chamber like the comparative example 1. A result is shown in Table 1.

[0034](Comparative example 4) The insulation reliability examination was done within the homoiothermal constant humidity chamber like the comparative example 3 except having processed the comb type pattern into the comb type pattern of a 25-micrometer pitch (the linewidth of 15 micrometers, the space width of 15 micrometers). A result is shown in Table 1.

[0035]As shown in Table 1, in Examples 1-8 of this invention, the insulation resistance value which far exceeds $1x10^{4}$omega after [whose] 1000-hour progress is a bad insulation judging standard was acquired. The insulation resistance value in front is an insulation resistance value at the time of 1000-hour progress. On the other hand, resistance fell to $1x10^{4}$omega which is a bad insulation judging standard at the time of 250 hours and 300-hour progress, respectively in the comparative examples 2 and 4.

[0036]

[Table 1]

	配線ピッチ（μm）	保持時間（hr）	絶縁抵抗（Ω）
実施例1	40	1000 以上	1×10^{11}
実施例2	25	1000 以上	1×10^{10}
実施例3	25	1000 以上	1×10^{10}
実施例4	25	1000 以上	4×10^{10}
実施例5	25	1000 以上	2×10^{10}
実施例6	25	1000 以上	8×10^{9}
実施例7	25	1000 以上	1×10^{11}
実施例8	25	1000 以上	1×10^{11}
比較例1	40	1000 以上	1×10^{9}
比較例2	30	250	1×10^{4}
比較例3	40	1000 以上	5×10^{9}
比較例4	30	300	1×10^{4}

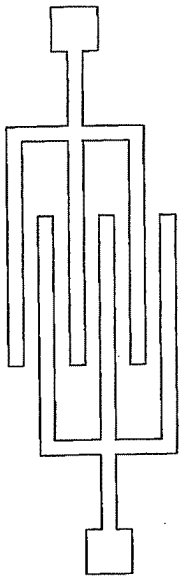
[0037]

[Effect of the Invention]By oxidizing the metal ion which remains slightly on the surface, and controlling ion migration by washing processing by the oxidizer of the surface after etching by this invention, as explained above. The metallizing copper polyimide wiring board which has the insulation reliability outstanding also at the time of fine wiring can be manufactured.

[Brief Description of the Drawings]

[Drawing 1]It is the comb type pattern used for the insulation reliability examination in the example of this invention, and the comparative example.

[Drawing 1]



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